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Some organic bases cause the dimerization of isocyanates. Under certain conditions, the dimers split into CO_2 and carbodiimides [1, 2]. In a search for such bases, we studied the reaction of acyl isocyanates with 2-picoline, 4-picoline, and 4-vinylpyridine. These picolines, similarly to pyridine [2], dimerize benzoyl isocyanate, while in the case of more electrophil-ic trichloroacetyl isocyanate, the reaction halts at the formation of N-[4-(2)methyl-1-pyrid-inocarbonyl]trichloroacetylamidates (Ia and Ib).



 $R = 2-Me(a), 4-Me(b), 4-CH=-CH_2(c).$

Amidates (Ia) and (Ib) are crystalline, extremely hygroscopic compounds which decompose by the action of atmospheric moisture to give picolines, trichloroacetamide, and CO₂. The IR spectra of (Ia) and (Ib) have characteristic bands at 1750, 1760 (O-C-N-C-O), 1620, 1640 cm⁻¹ (C=C and C=N). The strong band at 1750 and 1760 cm⁻¹ is characteristic for stretching vibrations of the urea C=O group. The shift toward higher frequencies indicates the presence of a positively charged ring nitrogen adjacent to the carbonyl group [3] and the position of this band depends on the extent of charge delocalization in the bipolar ions. The frequency of the carbonyl band diminishes with increasing charge delocalization. Comparison of $v_{C=O}$ for (Ia) and (Ib) with $v_{C=O}$ in N-acyl pyridinium salts (1745-1804 cm⁻¹) indicates considerable charge delocalization in (Ia) and (Ib). An analogous carbonyl band was seen in the IR spectra of bipolar ions obtained by the reaction of chlorosulfonyl isocyanate with pyridine and triethylamine [4].

Amidates (Ia) and (Ib) were studied by PMR spectroscopy (Table 1). Since the carbon atoms of the ring also participate in delocalization of the positive charge on the pyridinium ring nitrogen atom, the electron density on these atoms is reduced relative to the value in the neutral molecule. This results in deshielding of the ring protons. The data in Table 1 show that the greatest deshielding is found for H⁴ in (Ia) and H² and H⁶ in (Ib), i.e., those protons bound to carbon atoms having minimal π -electron density. The π -electron density on the carbon atoms in (Ia) and (Ib) is even less than in the starting compounds due to the electron-withdrawing effect of the positively charged ring nitrogen atom. The small value for $\Delta\delta$ for H⁶ in (Ia) may be attributed to the approximation of C⁶ to the methyl group which has an electron donor effect, while the π -electron density in 2-picoline itself is enhanced relative to that on C⁴.

Comparison of the IR and PMR spectra of the starting compounds, (Ia), (Ib), and the reaction mixtures of trichloroacetyl isocyanate with 2- and 4-picolines revealed a change over time for $\Delta\delta$ by 4-14 Hz (see Table 1) and a shift in the stretching band for the 0.5 M -0.5 fragment $\Delta\nu = 15-20$ cm⁻¹. The formation of (Ia) and (Ib) is apparently preceded by the formation of an n- π donor-acceptor complex. Phenyl and methyl isocyanates form such complexes with pyridine [6].

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Product or reaction mix- ture (in 10% acetone		Desi	hielding ∆	δ, Hz			1 I 1 I 1 I 1 I 1 I 1 I 1 I 1 I 1 I 1 I	Electron d and 4-pic	ensities of olines [5]	ı C atoms	in	Initial
solution)	H2	H ³	H ⁴	Ηs	θH	Me	C3	ů	ů	ů	ů	compound
(Ia)		27	33	29	12	18	0,956	1,025	0,960	1,020	0,979	2-Picoline
4-Picoline + CCl ₃ CONCO		23	28	24	œ	13						
(Ib)	68	58		58	68	22	0,982	1,022	0,941	1,022	0,982	4-Picoline
4-Picoline + CCl ₃ CONCO	61	44		44	61	14						

TABLE 1. Proton Deshielding ($\Delta\delta$, Hz) in (Ia), (Ib), and Reaction Mixtures and π -Electron Densities on the Carbon Atoms in 2- and 4-Picolines

The addition of trichloroacetyl isocyanate to the picolines in CCl₄ solution proceeds reversibly as indicated by the IR and PMR spectra. In addition to IR and PMR bands assigned to (Ia) and (Ib), such bands are found for the starting compounds. In acetonitrile solution, the equilibrium is shifted toward (Ia) and (Ib), which is apparently related to the participation of the solution in stabilization of the charges in the bipolar ions.

In addition to the reactions of acyl isocyanates with picolines, we also studied the reaction with 4-vinylpyridine, which has a reactive vinyl group in addition to a nucleophilic site (the nitrogen atom). We have previously shown that in nonpolar aprotic solvents such as CC14 and ether, the reaction of acyl isocyanates with 4-vinylpyridine proceeds by [2 + 4]addition to form 4-oxo-2-phenyl(trihalomethyl)-6-(4-pyridyl)-5,6-dihydro-1,3-oxazines, i.e., the addition proceeds at the vinyl group [7, 8]. Carrying out the reaction of trichloroacetyl isocyanate with 4-vinylpyridine in polar aprotic solvents such as CH₃CN, CH₂Cl₂ and ClCH₂CH₂Cl facilitates the formation of an N-substituted trichloroacetylamidate (Ic). The corresponding substituted 1,3-oxazine is formed in ~5% yield as indicated by IR spectroscopy. The IR spectra of (Ic) have bands at 1745 (0-C-N-C-O), 1635 (CH=CH₂), 3025, 3075 (ring =CH, CH=CH₂), and 925 1040 cm^{-1} (nonplanar vinyl CH and CH₂ deformation vibrations). Comparison of the PMR spectra of 4-vinylpyridine and (Ic) revealed that greatest deshielding is found for the protons at C² and C⁶ ($\Delta\delta$ 94 Hz), while the protons at C³ and C⁵ are less deshielded ($\Delta\delta$ 62 Hz). The downfield for the protons in the CH=CH₂ group is 22 Hz for H_R , 27 Hz for H_A , and 6 Hz for H_C. Thus, the direction for the addition of trichloroacetyl isocyanate to 4-vinylpyridine depends significantly on the nature of the solvent.

EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrometer in acetonitrile while the PMR spectra were taken on a Varian HA-100 spectrometer in CCl₄ and MeCN.

<u>N-(2-Methyl-1-pyridinocarbonyl)trichloroacetylamidate (Ia)</u>. A solution of 1.89 g trichloroacetyl isocyanate in 10 ml MeCN was added dropwise with stirring to a solution of 0.93 g 2-picoline in 20 ml MeCN at 0°C. After 24 h, two-thirds of the solvent volume was removed in vacuum and the residue was cooled to -40°C to produce a dark-yellow precipitate which was filtered and washed with cold ether, mp 93-96°C (dec.). The yield of (Ia) was 1.72 g (61%). Found: C 38.62; H 2.78; Cl 37.51%. CgH₇N₂O₂Cl₃. Calculated: C 38.36; H 2.48; Cl 37.83%. The crystals became dark and tarry upon standing for 48 h at 18-20°C.

<u>N-(4-Methyl-1-pyridinocarbonyl)trichloroacetylamidate (Ib)</u>. A solution of 2.05 g trichloroacetyl isocyanate in 15 ml CCl₄ was added dropwise with stirring to a solution of 1.0 g 4-picoline in 10 ml CCl₄. The precipitate formed was filtered after 0.5 h and washed with ether, mp 80-84°C (dec.). The yield of (Ib) was 2.5 g (81.9%). Found: C 38.50; H 2.70; Cl 37.58%. C₉H₇N₂Cl₃O₂. Calculated: C 38.36; H 2.48; Cl 37.83%.

The reaction of 4-picoline with trichloroacetyl isocyanate in MeCN was carried out similarly to that for the preparation of (Ia).

<u>N-(4-Vinyl-1-pyridinocarbonyl)trichloroacetylamidate (Ic)</u>. A solution of 2.46 g 4-vinyl-pyridine in 60 ml ClCH₂CH₂Cl was added dropwise to a solution of 4.42 g trichloroacetyl isocyanate in 10 ml dichloroethane (or MeCN or CH₂Cl₂). The precipitate formed was filtered off after 5 min, washed with MeCN and ether, and dried in a vacuum dessicator, mp 175-178°C (dec.). The yield of (Ic) was 5.67 g (78.9%). Found: C 41.02; H 2.61; Cl 36.02%. $C_{10}H_7N_2O_2$ -Cl₃. Calculated: C 40.88; H 2.38; Cl 36.18%.

CONCLUSIONS

Trichloroacetyl isocyanate reacts with 2- and 4-picolines to form substituted trichloroacetylamidates. Benzoyl isocyanate forms a dimer in the presence of picolines. Depending on the nature of the solvent, trichloroacetyl isocyanate adds to 4-vinylpyridine either at the vinyl group or at the ring nitrogen atom.

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REACTION OF PHENYL DITHIOBENZOATE AND N-BUTYLTHIOACETAMIDE

WITH N-NITROSOACETANILIDES

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In our previous work [1, 2], we showed that the aryl radicals which arise in the radical arylation of compounds containing the C=S group such as thioureas, thioamides, and esters of thiocarboxylic acids always add at the S atom to form intermediate radical-adducts of the type R- \dot{C} (X)SAr (X = NH₂, NHR, and OR). In many cases, these radicals may be detected by ESR spectroscopy by the use of spin traps and their subsequent chemical transformations may be followed by preparative methods.

In a continuation of this work, we studied the reaction of $p-MeC_6H_4$ radicals (Tol^{*}), generated by the decomposition of N-nitrosoaceto-p-toluidine (NAT), with the phenyl ester of dithiobenzoic acid PhC(S)SPh (I). This reaction proceeds at 20°C with virtually complete conversion of the starting dithioester; the products obtained and their yields (in % of theoretical yield) are given below



The high overall yield of products containing the STol group indicates that there is virtually complete addition of the tolyl radicals to the sulfur atom of the C=S group of the dithioester. The formation of 1,2-bisphenylthio-1,2-bistolylthio-1,2-diphenylethane (II) as SPh

the major product unequivocally indicates that the radical-adduct $PhC \begin{pmatrix} \bullet & & \\ &$

Dimerization as a pathway for the stabilization of radical-adduct A is noted for the first time in this reaction. In analogous reactions for thioamides and thioureas, the radical-adducts are stabilized by other pathways [1].

The formation of (III)-(VII) and the ratio of their yields may be explained assuming that the intermediate radical-adducts A not only dimerize but also undergo oxidation to radicals PhC(0)(SPh)STol(B). The possibility of such a reaction has been established by an ESR spectroscopic study of analogous radicals formed in the thermolysis and photolysis of acetophenone diphenylmercaptol [3]. In the reaction studied, the products of the decomposition of the acylating reagent (the N-nitroso compound) may act as the oxidizing agent. The fragmentation

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